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Self-assembly of chiral mesoionic heterocycles into smectic phases: a new class of polar liquid crystal

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Abstract—The molecular design, synthesis and characterization of the first examples of both classical and non-conventional chiral mesoionic (mesomeric + ionic) liquid crystals derived from sydnones are described. The occurrence of chiral smectic phases in these novel compounds was evidenced by optical microscopy, calorimetry and X-ray studies.

Liquid crystal (LC) phases are unique self-assembled structures characterized by both optical (Δn) and dielectric anisotropic ($\Delta\varepsilon$) properties that have been well exploited in various applications especially in display device technology.[1] The most popular examples are the conventional thermotropic LCs, in particular covalent rod-like (calamitic) molecules, which prefer an arrangement in layered (smectic: Sm) and/or non-layered (nematic: N) fluid structures. Mesogens possessing molecular chirality,[2,3] self-organize to form LC chiral bulk aggregates such as helical structures of the chiral nematic (N*) or chiral smectic C (SmC*) and chiral smectic A (SmA*) phases. These features have led to the discovery of thermochromism, ferroelectricity, antiferroelectricity, pyroelectricity and electro-clinism, etc. Therefore a large number of covalent (polar or apolar) optically active calamitic LCs have been engineered and synthesized especially in the context of ferroelectric LCs.[3]

The converse versions of chiral covalent LCs are the ionic LCs in which charge separation occurs. They represent an important class of amphiphilic LCs because they display intrinsic phase chirality in their lyotropic forms.[2a,4] Recently there has been a resurgence in the design and synthesis of a class of LCs in which the anisotropic shape of the molecules is distorted away from the classical rod- or disc-shape,[5] these are termed 'non-conventional LCs', some examples of which are dimers, bent-core molecules, polycatenars, dendrimers, etc. Hitherto, optically active, classical or non-conventional mesogens that have an inherently mesomeric (covalent) and ionic hybrid nature were unknown.

Mesoionic (mesomeric + ionic) compounds are a class of five-membered heterocycles, which cannot be represented *satisfactorily* by any one neutral or polar structure but only as hybrids of polar structures.[6] Sydnones, for example, 3-phenylsydnone (Scheme 1, **1a**), which conform to the description above, are the most comprehensively investigated mesoionic systems mainly due to the biological significance associated with their planar aromatic character[6b–d] and interesting physical and chemical properties. Remarkably, their highly polarized yet net neutral electrical character and high dipole moments[6h,i] (μ = 5–6 Debye) are promising in the context of the properties of LCs. As part of our ongoing programme to design and synthesize technologically important thermotropic LCs,[7] we set out to synthesize chiral mesogenic sydnones to furnish a new class of functional materials. Thus on the molecular or segmental level, the introduction of a sydnone ring could

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Keywords: Chirality; Mesoionic; Liquid crystals; Smectic.

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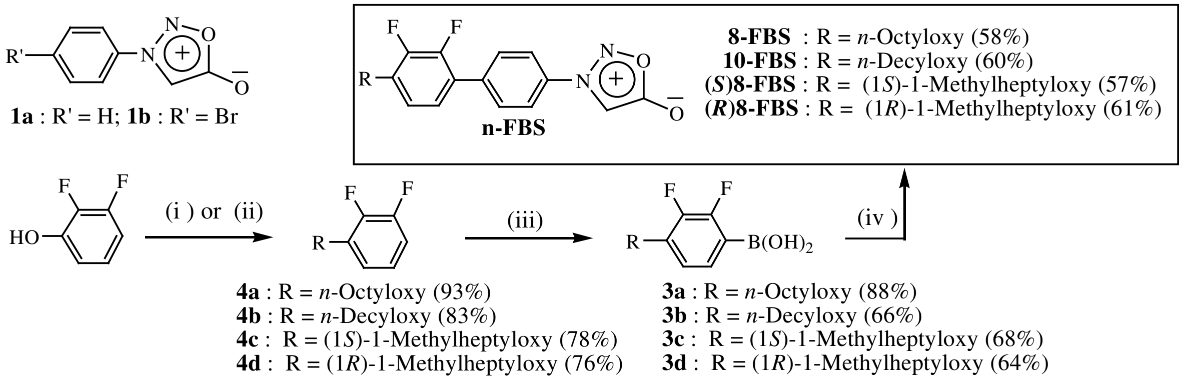

Scheme 1. Reagents and conditions: (i) 1-bromooctane/decane, anhyd K_2CO_3, acetone, reflux, 12 h; (ii) (*R*)/(*S*)-2-octanol, Ph_3P, DEAD, THF, 10–15 °C to rt, 12 h; (iii) *n*-BuLi, THF, $[(CH_3)_2CHO]_3B$, −70 °C, aq HCl; (iv) **1b**, $[(C_6H_5)_3P]_4Pd$, Na_2CO_3, DME, reflux, 12 h.

produce structures with properties between those of covalent and ionic LCs.

Our first targets were both conventional and non-conventional optically active mesoionic LCs. It would be advantageous if the molecular design directed the self-assembly of the molecules into smectic structures. In view of this, for conventional systems a biphenyl core substituted with a ‘floppy’ tail and a polar sydnone moiety as terminal substituent appeared to be an ideal target.[8a] Furthermore, earlier investigations have revealed that lateral fluoro-substituents in rigid (e.g., biphenyl or terphenyl) cores help in reducing the melting point of the parent system.[9] It is also well established that the transverse polarity and hence dielectric biaxiality of smectic LCs can be increased by the incorporation of lateral fluoro-substituents in the core. Thus, a laterally fluoro-substituted biphenyl core with a chiral flexible tail and a sydnone ring as terminal entities appeared to be favourable systems. Initially, achiral systems were prepared and their LC behaviour was found to agree with the molecular design mentioned above. Both achiral (**8-FBS** and **10-FBS**) and chiral [(***S***)**8-FBS** and (***R***)**8-FBS**] target fluorobiphenyl-sydnones (***n*-FBS**), were prepared by Suzuki coupling[8c] of 3-(4-bromophenylsydnone) **1b** with 2,3-difluoro-4-alkoxyphenylboronic acids[8a,b] (**4a–d**) as shown in Scheme 1.

Recently chiral dimers possessing a cholesteryl ester unit as the chiral entity joined to other aromatic mesogens through a polymethylene spacer have attracted attention as they show remarkable mesomorphic properties.[5b–d] In particular, a dimer formed by joining a cholesteryl ester moiety to a Schiff's base or salicylaldimine entity through a paraffinic spacer supports the formation of smectic structures.[5d] Therefore we aimed to prepare chiral mesoionic dimers by covalently connecting a cholesteryl ester entity to mesoionic salicylaldimines through either an odd or an even paraffinic spacer. Four dimers **DS-3**, **DS-4**, **DS-5** and **DS-7** were synthesized by condensing cholesteryl *n*-(3-hydroxy-4-formylphenoxy)-alkanoates[5d] (**5a–d**) with 3-(4-aminophenyl)sydnone[6j] **2** as depicted in Scheme 2.

The target compounds thus prepared were characterized by spectroscopic and elemental analyses.[†] The liquid crystalline properties of the target molecules were investigated primarily with optical polarizing microscopy (OPM) and differential scanning calorimetry (DSC). The results are summarized in Table 1. Compounds **8-FBS** and **10-FBS** displayed an enantiotropic SmA phase as shown by the OPM observation of the characteristic focal-conic texture in slides treated for planar orientation and a psuedoisotropic texture when treated for homeotropic geometry. This observation supports our

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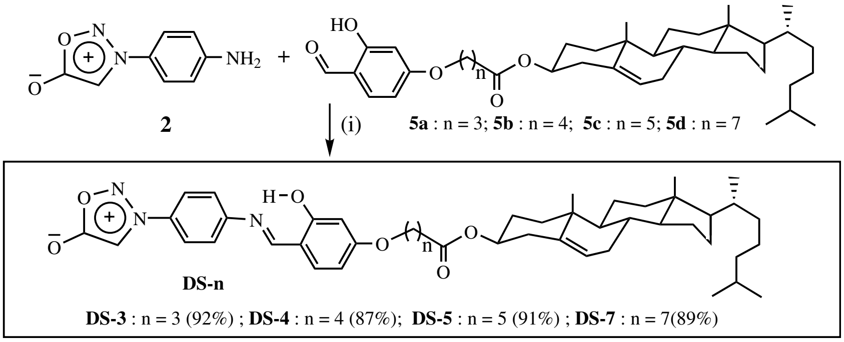
[†] Molecular structural characterization data for selected compounds: (***S***)**8-FBS**: A brownish solid; mp: 50–51 °C; R_f: 0.48 in 50% EtOAc–hexane; $[\alpha]_D^{23}$ −22 (*c* 1, $CHCl_3$); UV–vis ($CHCl_3$): $\lambda_{max} = 296$ nm, $\varepsilon = 2.53 \times 10^3$ L mol^{-1} cm^{-1}; IR (KBr pellet): ν_{max} cm^{-1} 3116, 2930, 2858, 1759, 1631, 1056 and 850; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.78 (s, 4H, Ar), 7.13 (dt, $J = 8$ and 2.2 Hz, 1H, Ar), 6.86 (dt, $J = 7.2$ and 2.2 Hz, 1H, Ar), 6.75 (s, 1H, sydnone-H), 4.46 (m, 1H, 1 × –CH), 1.82–1.46 (m, 10H, 5 × CH_2),1.38 (d, $J = 6$ Hz, 3H, 1 × CH_3) and 0.89 (t, $J = 6.6$ Hz, 3H, 1 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.94, 149.39 (dd, $^1J_{C\text{-}F} = 206$ Hz, $^2J_{C\text{-}F} = 13$ Hz), 147.90 (d, $^2J_{C\text{-}F} = 12$ Hz), 142.7 (dd, $^1J_{C\text{-}F} = 246$ Hz, $^2J_{C\text{-}F} = 14$ Hz), 139.58, 133.85, 130.44, 123.52, 121.46, 120.43 (d, $^2J_{C\text{-}F} = 10.8$ Hz), 112.08, 93.50, 76.99, 36.42, 31.78, 29.22, 25.40, 22.60, 19.83 and 14.06; MS (FAB+): *m/z* for $C_{22}H_{25}F_2N_2O_2$ (M+1), calcd: 403; found: 403; Elemental analysis: calculated (found): C, 65.66 (65.73); H, 6.03 (6.01); N, 6.5 (6.96). **DS-5**: A yellow solid; mp: 215 °C (decomposes); R_f: 0.40 in 20% EtOAc–hexane; $[\alpha]_D^{23}$ 8.3 (*c* 1, $CHCl_3$); IR (KBr pellet): ν_{max} in cm^{-1} 2948, 2867, 2364, 1732, 1624, 1593, 1119 and 835; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.04 (s, 1H, 1 × –OH), 8.55 (s, 1H, 1 × –CH=N), 7.76 (d, $J = 8.8$ Hz, 2H, Ar), 7.44 (d, $J = 8.8$ Hz, 2H, Ar), 7.31 (d, $J = 8.3$ Hz, 1H, Ar), 6.71 (s, 1H, 1 × –CH), 6.53 (m, 2H, Ar), 5.37 (br d, $J = 4.2$ Hz, 1H, 1 × olefinic), 4.63 (m, 1H, 1 × –CHOCO), 4.03 (t, $J = 6.4$ Hz, 2H, 1 × –OCH_2), 2.33 (m, 4H, 2 × allylic methylene), 2.02–1.10 (m, 32H, 13 × –CH_2, 6 × –CH), 1.02 (s, 3H, 1 × –CH_3), 0.91 (d, $J = 6.5$ Hz, 3H, 1 × CH_3), 0.87 (d, $J = 1.7$ Hz, 3H, 1 × CH_3), 0.85 (d, $J = 1.7$ Hz, 3H, 1 × CH_3) and 0.68 (s, 3H, 1 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.92, 164.58, 163.97, 163.84, 152.65, 139.76, 134.28, 122.78, 122.66, 122.45, 112.76, 108.30, 101.74, 93.35, 73.92, 68.13, 56.77, 56.27, 50.16, 42.39, 39.83, 39.57, 38.24, 37.07, 36.66, 36.25, 35.81, 34.57, 31.96, 28.76, 28.23, 28.03, 27.90, 25.58, 24.76, 24.32, 23.88, 22.55, 21.10, 19.33, 18.76 and 11.89; MS (FAB+): *m/z* for $C_{48}H_{66}N_3O_6$ (M+1), calcd: 780.5; found: 781; Elemental analysis: calculated (found): C, 73.91 (73.65); H, 8.40 (8.62); N, 5.39 (5.55).



Scheme 2. Reagents and conditions: EtOH, AcOH (trace), reflux, 4 h.

Table 1. Phase sequence, transition temperatures (°C)[a] and enthalpies (J/g) of achiral and chiral mesoionic compounds

Compd	Heating	Cooling
8-FBS	Cr 90.1 (26.7) SmA 136.4 (6.8) I	I 135.3 (6.5) SmA 77.8 (40.3) Cr
10-FBS	Cr 92.4 (42.8) SmA 144.8 (6.7) I	I 143.2 (6.5) SmA 79.1 (27.6) Cr
(***S***)**8-FBS**	Cr 51 (29.4) I	I 49.1 (0.8) SmX* 30 (25.3) Cr
(***R***)**8-FBS**	Cr 47.8 (20.9) I	—
(**DS-3**)	Cr 230[b] SmA* 265[c]	—
(**DS-4**)	Cr 162[b] SmA* 210[c]	—
(**DS-5**)	Cr 170[b] SmA* 215[c]	—
(**DS-7**)	Cr 242[b] SmA* 270[c]	—

Cr = crystal; SmA = smectic A; SmA* = chiral smectic A; SmX* = unknown chiral smectic; I = isotropic phase.

[a] Peak temperatures in the DSC thermograms obtained during first heating and cooling cycles at a rate of 5 °C/min.

[b] Microscopic observation indicated the Cr–SmA phase transition, while a precise enthalpy value could not be measured due to the inconsistent base line of the thermogram at this temperature.

[c] The transition from SmA–I could not be ascertained by either microscopy or calorimetric techniques, as the sample showed thermal degradation above this temperature.

molecular design principle for the formation of smectic phases.

Of the target optically active substances, the (*R*)-enantiomer, (***R***)**8-FBS** surprisingly, was found to be non-mesomorphic while its optical isomer (***S***)**8-FBS** displayed a smectic phase, which we abbreviate as SmX*. With slides treated for planar orientation, on formation from the isotropic phase, the SmX* phase appeared with small batonnets, which grew anisotropically until they merged, forming a broken focal-conic (fan-shaped) texture (Fig. 1). Further dechiralization lines were seen on top of the focal-conics. With homeotropic boundary conditions, a cloudy texture appeared. These observations suggest the phase to be a chiral tilted one with a macroscopic helical arrangement of molecules as in the case of a chiral smectic C (SmC*) phase. The helix occurs as a result of a gradual change in molecular tilt direction from layer to layer, about an axis perpendicular to the layer planes. It is well known that such helical structures can be unwound by the application of an electric field to obtain ferroelectric switching. To confirm such behaviour, electrical switching investigations were carried out in the SmX* phase. A cell was constructed using two indium tin oxide (ITO) coated glass plates pre-treated with a polyimide solution, which enables the molecules to align homogeneously. The sample in its isotropic phase was transferred into the cell by capillary action and cooled slowly. After transition to the SmX* phase, a low frequency AC triangular wave electric field was applied and increased gradually. Surprisingly, even with quite large voltages, no switching was observed, which is unlikely in the SmC* phase. On the other hand, X-ray diffraction (XRD) studies (see below) showed that the smectic planes are fluid in nature. Thus it is possible that the phase is of a smectic I* or smectic F* type, which has additional bond orientation order.

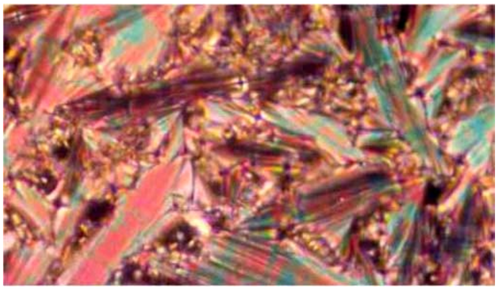


Figure 1. Polarizing photomicrograph of the planar texture for the SmX* phase of (***S***)**8-FBS** at 40 °C (magnification 300×).

To ascertain the structure of the phase, XRD studies were performed using an image plate arrangement; the sample was contained in a Lindemann capillary tube and was not oriented. The XRD pattern obtained at 45 °C, along with the extracted intensity versus 2θ profile is shown in Figure 2. Two sharp peaks at small angles (corresponding to 30.4 and 15.5 Å spacings) and a diffuse peak at wide angle (4.4 Å) were obtained. The latter is characteristic of liquid-like order within the smectic planes. The sharp peak at 30.4 Å represents the layer thickness *d*, with a value greater than the estimated molecular length (*l*) of 22 Å indicating a partial bilayer structure similar to the $\mathrm{SmA_d}$ phase formed by polar mesogens.[9] The preliminary XRD result suggested the phase to be a partially bilayered one with either a SmC* or a hexatic (SmI* or SmF*) structure. The monotropic nature of the SmX* phase and the strong tendency of the sample to crystallize in the required

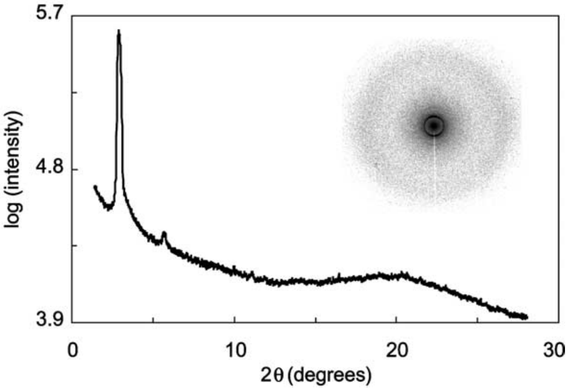


Figure 2. XRD intensity profile of an unoriented sample of (***S***)**8-FBS** in the SmX* phase obtained at 45 °C.

temperature range prevented us from performing a detailed structural investigation.

The thermal behaviour of the dimeric compounds **DS-3** to **DS-5** was somewhat unsatisfactory. The compound **DS-3** placed between the untreated slides, melted at about 230 °C to a mesophase with a non-characteristic birefringent texture in some areas and a dark field of view in a large portion of the slide. On mechanical shearing, it took on a pseudo-isotropic texture. On further heating (above 265 °C), the sample tended to thermally degrade. When examined with slides treated for a homogeneous condition, focal-conics as well as polygons were seen in some regions suggesting the phase to be SmA. This was evidenced by the observation of a dark field of view in slides treated for homeotropic orientation. Similar behaviour was noticed for the other dimers.

In conclusion, we have reported the first examples of optically active mesoionic mesogens. In the course of this study mesoionic chiral smectic phases have been realized. With inherent polar character coupled with mesomorphic behaviour, they form a unique class of chiral thermotropic liquid crystals, and deserve systematic and extensive investigations.

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